


19 
Europäisches Patentamt
European Patent Office
Office européen des brevets



11 Publication number : 0 433 258 A1

12
EUROPEAN PATENT APPLICATION

21 Application number : 90850402.0

51 Int. Cl.⁵ : D21C 3/00, D21C 9/00

22 Date of filing : 11.12.90

30 Priority : 12.12.89 FI 895930

43 Date of publication of application :
19.06.91 Bulletin 91/25

84 Designated Contracting States :
DE FR GB SE

71 Applicant : ENSO-GUTZEIT OY
Tutkimuskeskus
SF-55800 Imatra (FI)

72 Inventor : Vaheri, Marja
Lystimäenkuja 1 A
SF-02210 Espoo (FI)
Inventor : Ryynänen, Helena
Kelohongantie 14 E 27
SF-02120 Espoo (FI)
Inventor : Kunnäs, Aino
Asomäentie 11-13 as. A
SF-55120 Imatra (FI)

74 Representative : Fogelberg, Lennart et al
STENHAGEN PATENTBYRA AB Box 17 709
S-118 93 Stockholm (SE)

54 Procedure for the production of pulp.

57 The invention relates to a procedure for the production of mechanical pulp from a fibrous product. To improve the strength properties, the fibrous product is subjected to a chemical and/or enzymatic treatment in which a binding agent is linked with the lignin in the fibrous product. The bond between the binding agent and the fibre is created either by using oxidizing enzymes or oxidizing chemicals producing radicals.

EP 0 433 258 A1

PROCEDURE FOR THE PRODUCTION OF PULP

The present invention relates to a procedure for the production of mechanical pulp from a fibrous product.

The production of mechanical pulp from a fibrous product, such as whole wood, wood chips, chips or refined pulp is mainly implemented by mechanical methods. The production of mechanical pulp is based on the utilization of friction. Energy is transferred to the wood in a compress-release process generating frictional heat which softens the wood so that individual fibres can be released.

The object of pulp production is to reduce the wood structure into fibres and to process the fibres so as to make them fit for use as raw material in the manufacture of paper or cardboard. The natural function of wood fibres is exactly the opposite of this object, i.e. to form a supporting structure as strong as possible.

The fibres are bound together by an intermediate lamella which mainly consists of lignin. In the manufacture of chemical pulp, the intermediate lamella is dissolved using chemicals. The fibres can be separated undamaged, but besides lignin, even some of the hemicellulose in the wood is dissolved. Only about half the fibre content of the wood can be retrieved, i.e. the yield is 50%. In mechanical methods, the lignin is softened by means of water, heat and repeated application of mechanical stress so that the fibres can be "torn" apart. The fibres are disrupted in the process, but the yield is as high as 96-98%.

Mechanical pulps are produced by separating the fibres, which are bound together in the wood, either by grinding the wood against a grinding stone or by refining wood chips in disc refiners. The former type of pulp is generally called groundwood pulp and the latter type is called refiner mechanical pulp. In the more advanced forms of the refining method, heat (TMP) and possibly even chemicals (CTMP) are used.

The yield in the mechanical pulp production methods is high. Only a few per cent of the weight of the wood is lost. Therefore, the cost of the wood as per ton of pulp is low. On the other hand, the energy consumption is high, and the energy costs are an important factor. Also, the vigorous mechanical treatment causes fibre damage, reducing the strength of the paper produced from the pulp, which is why the use of mechanical pulp is limited to certain products of a lower quality requirement level.

In earlier research it has been established that the strength properties of mechanical pulp can be influenced by the degree of refining and by mechanically adding binding agents or softwood sulphate pulp into the mechanical pulp.

Increasing the degree of refining involves the disadvantages of increased production costs and a low processability (anhydrous quality) of the refined product. Adding sulphate pulp into mechanical pulp is generally avoided as far as possible because of the costs.

Binding agents are used to strengthen the bonds between the fibres. The strength properties of paper are largely dependent on these bonds. By far the most commonly used dry strength bonding agent is cationic starch. For wood pulps with a high content of fine fibres and fillers, the amount of starch needed is 0.5 - 2%. If starch is used in amounts exceeding this, the operability of the machine as well as the paper quality practically always decline.

Thus, the object of the present invention is to create a procedure by which the strength properties of mechanical pulp can be improved. The invention is characterized in that the fibrous product is subjected to a chemical and/or enzymatic treatment in which a binding agent is linked with the lignin in the fibrous product. According to the invention, it has been established that, by using an enzyme and/or a chemical, it is possible to add a suitable molecule to the free and easily oxidizable groups of lignin. If a binding agent is united with the fibre surface in a chemical reaction, it will improve the strength properties of the fibre. If necessary, the amount of binding agent used can be increased without producing adverse effects. The bond between the binding agent and the fibre is created either by using oxidizing enzymes or oxidizing chemicals producing radicals.

The strength properties can be improved with an enzyme treatment in which mechanical pulp is treated in the presence of certain substances, e.g. carbohydrates and proteins, containing hydrophobic groups, with enzymes acting on lignin. Chemical bonding can be successfully achieved in mechanical pulps produced by different methods on condition that lignin or its derivatives are present in the reaction mixture.

The purpose of the oxidation treatment, either enzymatic or chemical, is to produce in the lignin of the fibre a radical with which the binding agent is linked by a chemical bond so that the strength properties of the pulp are substantially improved. The substance used for producing a radical is preferably laccase, lignin peroxidase, manganese peroxidase or an oxidizing chemical producing radicals, e.g. chlorine dioxide, ozone or hydrogen peroxide together with ferro ions. Examples of suitable enzymes are those produced by white rot fungi, e.g. the laccase produced by the fungus *Coriolus versiculus*. The pulp temperature during the enzyme treatment may be in the range 10-90°C, preferably 40-70°C, and the pH in the range 2.0-10.0, preferably 4.0-8.0. In addition, the redox potential must be relatively high, in enzyme treatment approx. 100-600 mV, preferably 300-500 mV, and in chemical treatment above 200 mV.

In the following, the invention is described in detail by the aid of examples of embodiments based on laboratory tests.

Example 1.

5

20 g (abs.k) of reclaimed paper pulp made of reclaimed paper and cardboard was diluted with water until a consistency of 2.5% was reached.

The mixture was heated to 40°C. Next, starch (Amisol 202) in an amount of 5% was added into the mixture, which was stirred properly. Water-diluted chlorine dioxide in a quantity of 0.5% of the amount of pulp was added into the reaction mixture. The reaction was allowed to continue at 40°C for two hours.

10

After this, the pulp was washed with a 20-fold amount of water, whereupon it was concentrated and analyzed.

The results reflecting the strength of the pulp are presented in Table 1.

15

In addition to the test described above (test 5), three reference tests (tests 1, 2 and 3) and two additional tests (tests 4 and 6) were carried out. The results of these are likewise presented in Table 1. The tests were performed as follows :

20

25

30

35

40

45

50

55

TABLE 1

| | TEST 1 reference | TEST 2 reference | TEST 3 reference | TEST 4 | TEST 5 | TEST 6 |
|---|---------------------|---------------------|---------------------|--------|--------|--------|
| C10 ₂ (% of pulp) | 0 | 0 | 0 | 0.5 | 0.5 | 0.5 |
| Starch (% of pulp) | 0 | 5 | 10 | 0 | 5 | 10 |
| Consistency % after addition of liquid | 2.0 | 2.2 | 2.0 | 2.5 | 2.2 | 2.0 |
| pH | 5.9 | 5.9 | 6.1 | 5.4 | 5.3 | 5.3 |
| Bonding strength (KL 130:65) | 68.7 | 91.2 | 104.7 | 70.0 | 118.5 | 145.2 |
| Strength increase due to oxidizing reaction (%) | | | | 1.9 | 30.0 | 38.7 |
| Strength increase due to starch | | 32.8 | 52.4 | | | |
| Common effect of oxidiz- ing reaction and starch on strength increase (%) | | | | | 72 | 111.1 |

Test 1 (reference) : The pulp was not treated with chlorine dioxide and no starch was added to it. In other respects the implementation and analysis of the test corresponded to the test described above (test 5).

Test 2 (reference) : No chlorine dioxide treatment of the pulp was performed. In other respects the implementation and analysis of the test corresponded to the test described above (test 5).

Test 3 (reference) : No chlorine dioxide treatment was performed. Starch was added to the pulp in an amount of 10% of the amount of pulp.

Test 4 : The pulp was treated with chlorine dioxide, but no starch was added. In other respects the implementation and analysis of the test corresponded to the test described above (test 5). The procedure represented by this test belongs to the sphere of the present invention.

Test 6 : The pulp was treated with chlorine dioxide after a starch addition of 10% of the amount of pulp. In other respects the implementation and analysis of the test corresponded to the test described above (test 5). The procedure represented by this test belongs to the sphere of the present invention.

Example 2.

Unbleached TMP pulp was washed with ion-exchanged water and centrifugalized. The pulp was buffered with a Na citrate buffer, diluted to a consistency of 2.5% and heated to 40°C. Starch (oxidized, medium cationic) was added to the pulp in an amount of 5%, and the pulp was stirred properly. Laccase (activity 630 U/ml) diluted with water was added to the mixture in an amount of 0.1% of the amount of mixture, and the pulp was stirred carefully. The enzymatic reaction was allowed to continue for two hours at a temperature of 40°C. The pulp was stirred periodically during this time. At the end of the reaction the pulp was washed.

After the washing, the enzyme activity was destroyed by a 10-minute heat treatment at 80-85°C. Finally, the pulp was concentrated, centrifugalized and homogenized.

100-g sheets (SCAN-67) were produced from the pulps, and the sheets were tumble dried. The paper technical properties of the sheets were determined in accordance with the SCAN standards.

The results reflecting the strength of the pulp are presented in Table 2.

In addition to the test described above (test 2), a reference test (test 1) and two additional tests (tests 3 and 4) were carried out. The results of these are likewise presented in Table 1. The tests were performed as follows :

Test 1 (reference) : The pulp was not subjected to an enzyme treatment and no starch was added to it. As for the washing of the pulp and the analyses, the test corresponded to that described above (test 2).

Test 3 : The pulp was subjected to an enzyme treatment after peptone, instead of starch, in an amount of 5% of the amount of pulp had been added into the reaction solution. In all other respects, the treatment corresponded to that described above (test 2). The procedure represented by this test belongs to the sphere of the present invention.

Test 4 : Instead of an enzyme treatment, the pulp was subjected to an oxidizing chlorine dioxide treatment. The amount of chlorine dioxide used was 0.1% of the amount of pulp. In all other respects, the treatment corresponded to that described above (test 2). The procedure represented by this test belongs to the sphere of the present invention.

It is obvious from the results that the strength can be increased in the same way regardless of whether the oxidizing agent is chlorine dioxide or laccase. The results also indicate that, besides starch, peptone, too, can be used together with an oxidizing treatment to increase the strength of the pulp.

It can be seen from the results that the mere addition of starch as a binding agent increased the strength as expected, but the increase in strength was clearly larger in the cases where the pulp had been subjected to an oxidizing treatment as provided by the invention.

It is obvious to a person skilled in the art that the invention is not restricted to the embodiment example described above, but that it may instead be varied within the scope of the following claims.

TABLE 2

| | TEST 1 (reference) | TEST 2 | TEST 3 | TEST 4 |
|-----------------------------|-----------------------|--------|--------|--------|
| Laccase % of pulp | - | 0.1 | 0.1 | |
| C10 ₂ % of pulp | - | - | - | 0.1 |
| Starch % of pulp | - | 5 | - | 5 |
| Peptone % of pulp | - | - | 5 | - |
| Freeness CSF (ml) | 40 | 39 | 30 | 45 |
| Tensile index Nm/g | 44.6 | 55.0 | 53.3 | 54.0 |
| Increase in strength (%) | | 23.3 | 19.5 | 21.1 |

Claims

1. Procedure for the production of mechanical pulp from a fibrous product, characterized in that the fibrous product is subjected to a chemical and/or enzymatic treatment in which a binding agent is linked with the lignin in the fibrous product.
2. Procedure according to claim 1, characterized in that, during the chemical and/or enzymatic treatment of the fibrous product, radicals are produced in the lignin in the fibrous product, the binding agents being linked with the radicals by chemical bonds.
3. Procedure according to claim 1 or 2, characterized in that the binding agent is a hydrophilic substance, preferably a hydrocarbonate and/or a protein.
4. Procedure according to any one of the preceding claims, characterized in that the substance used for producing a radical is an oxidizing enzyme and/or an oxidizing chemical producing radicals, preferably laccase, lignin peroxidase, manganese peroxidase, hydrogen peroxide together with ferro ions, chlorine dioxide or ozone, used either by themselves or in mixtures.
5. Procedure according to any one of the preceding claims, characterized in that the enzyme treatment is performed within a temperature range of 10-90°C, preferably 40-70°C, and at a pH of 2.0-10.0, preferably 4.0-8.0.
6. Use of enzymes and/or chemicals acting on lignin, together with binding agents, to increase the strength properties of pulp in the manufacture of mechanical pulp.
7. Use of an enzyme and/or chemical according to claim 6 to improve the strength properties in the manufacture of mechanical pulp when oxidizing enzymes and/or oxidizing chemicals producing radicals are used.
8. Use of a binding agent according to claim 6 to improve the strength properties in the manufacture of mechanical pulp, the binding agents used being preferably hydrocarbonates and/or proteins.
9. Use of laccase, lignin peroxidase, manganese peroxidase, hydrogen peroxidase together with ferro ions, chlorine dioxide, ozone or mixtures of these according to claim 6 to improve the strength properties in the manufacture of mechanical pulp.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 85 0402

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|--|--|--|---|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claims | CLASSIFICATION OF THE APPLICATION (Int. Cl.5) |
| X | WO-A-8700564 (REPLIGEN CORPORATION) * page 3, line 17 - page 5, line 25 * * page 7, line 30 - page 8, line 14 * * page 20, lines 12 - 16; claims 1, 9, 10 * --- | 1, 3-9 | D21C3/00 D21C9/00 |
| A | BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY, vol. 52, no. 8, February 1982, APPLETON US page 933 Samuelsson L. et al.: "Influence of some chemical and radiative treatments on strength versus energy relationship in mechanical pulping." * abstract * | 1, 4, 6, 7, 9 | |
| A | WO-A-8803190 (CALL HANS-PETER) * claims 1, 4, 6-9, 12 * ----- | 1, 4-7, 9 | |
| | | | TECHNICAL FIELDS SEARCHED (Int. Cl.5) |
| | | | D21C |
| The present search report has been drawn up for all claims | | | |
| Place of search THE HAGUE | | Date of completion of the search 26 FEBRUARY 1991 | Examiner BERNARDO NORIEGA F. |
| CATEGORY OF CITED DOCUMENTS | | T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document | |
| X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document | | | |

EPO FORM 1503 (01.92) (P0401)